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THE INFLUENCE OF TESTING METHODOLOGY AND CHANGES OF MICROSTRUCTURAL PARAMETERS ON RESISTANCE OF DUPLEX STEEL TO SULPHIDE STRESS CRACKING

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The paper is focused on the evaluation of duplex ferritic-austenitic steel resistance to sulphide stress cracking (SSC). The testing was performed in accordance with the NACE TM 0177 Standard using tensile tests and four-point bending tests. The steel was always tested in two different structural states, in the as-received state (marked as AR), and after laboratory annealing by the mode of 800 °C/5h/air (marked as AN). Microstructure of steel in the AR state was formed by ferrite and austenite, the AN state was characterized by an disintegration of the part of ferrite and by formation of brittle σ phase. The aim of this study was to evaluate the effect of testing methodologies and changes of microstructural parameters of duplex steel resistance to SSC.

Key words: sulphide stress cracking (SSC), testing methods, duplex steel, mechanical properties, microstructure

INTRODUCTION

Sulphide stress cracking is a problem commonly affecting one major sector – the petrochemical industry. Petroleum and natural gas are very often contaminated by hydrogen sulphide. During corrosion reaction of steel with the given medium an atomic hydrogen is being developed, which can be absorbed by the steel and at specific conditions it may cause cracking, or even complete destruction of pipelines, pressure vessels, etc. [1, 2].

The problem of the negative effects of hydrogen sulphide in the oil industry has become more topical, since it is necessary to carry out still deeper and deeper wells to access oil and natural gas deposits. Certain role is also played by the fact that the production is usually concentrated into more polluted localities (also by hydrogen sulphide), because the better deposits were already extracted [1]. In this connection demand of oil companies for steels, which are sufficiently resistant to acidic environments continuously increases [3-5]. Testing the resistance of steels to SSC is specified by the NACE TM 0177 Standard [6], which describe a variety of testing procedures, the choice of which depends on operational requirements.

Duplex ferritic-austenitic steels belong to some of the best products of protection against corrosion with the longest service life. The balanced portion of ferritic-austenitic structure ensures their high utility value. Lower nickel contents compared to austenitic steels then makes these steel very interesting also from a perspective of price [7-10].

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EXPERIMENTAL MATERIAL

Duplex ferritic-austenitic steel was chosen for the experiment and was delivered in the form of sheet with thickness of 12 mm. Table 1 shows the chemical composition of the steel. Resistance of the steel to SSC was tested in two states, namely the as-received state (marked as AR), and the state after laboratory annealing by the mode 800 °C/5h/air (marked as AN). Microstructural analysis of the steel after electrolytic etching in 20 % NaOH was performed using a ZEISS NEOPHOT 32 light microscope and it is documented in Figure 1. Structure of the state AR was ferritic-austenitic, the volume fraction of both phases determined by image analysis using Image-Pro Plus software package was approximately 60 % of ferrite and 40 % of austenite (Figure 1a). After the laboratory annealing (AN) it was possible to observe an intense precipitation of brittle σ phase at the boundary ferrite/austenite, see Figure 1b. Volume fraction of σ phase was approximately 8 %, and the distribution was homogeneous throughout the sample volume. Very similar content of σ-phase was found

Table 1 **Chemical composition of the steel / wt.%**

C	Cr	Ni	Mo	Mn
0,019	21,30	4,92	2,86	1,04
Si	P	S	Cu	V
0,24	0,023	0,014	0,079	0,05

Table 2 **Mechanical properties of the steel in longitudinal direction**

state of steel	$R_{p0.2}$ /MPa	R_m / MPa	A_5 / %	Z / %
AR	455	668	45.5	81
AN	423	743	29	18

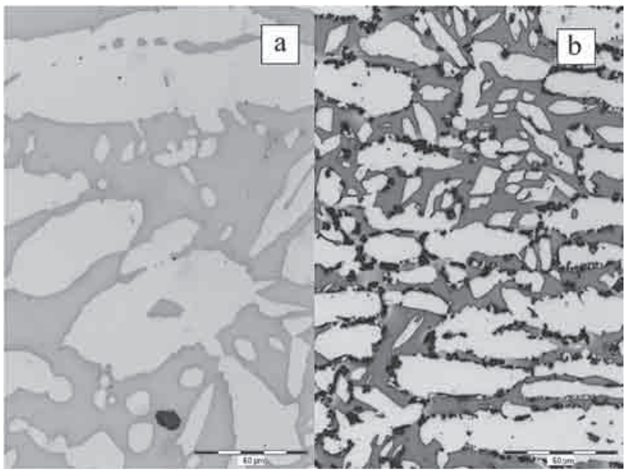

Figure 1 Microstructure of duplex steel in the as-received state (a) and in the state after laboratory annealing (b), etched by NaOH

by Michalska after annealing of the same kind of duplex steel at 750 °C for 5 hours [11].Table 2 presents the mechanical properties of the studied steel. It is evident that in the case of precipitation of σ phase (AN), significant deterioration of plastic characteristics and increased tensile strength took place compared to the AR state.

EXPERIMENTAL PROCEDURE AND OBTAINED RESULTS

Experiments were realized in accordance with the NACE TM 0177-2005 Standard. Exposition of specimens was carried out in the test solution A for a period of 720 h [6].

Specimens were loaded in accordance with the ASTM G49-85 [12] and ASTM G39-99 Standards [13]. Altogether 24 specimens were tested. 12 specimens with a diameter of 3 mm and the initial measured length of 15 mm were subjected to tensile load. The second half of the specimens with length of 115 mm, width of 15 mm and thickness of 5 mm was loaded by the four-point bending.

For objective comparison of both testing methods the parameters of loading were chosen identically, see Table 3. During the standard time of testing (720 hours) not a single test specimen did break. Observations performed by stereomicroscope at tenfold magnification also did not identify any surface defects. Metallographic polished sections were therefore prepared on the exposed parts of the specimens in the longitudinal direction. Microstructure of the samples was then developed by the etching agent V2A and evaluation on JEOL JSM-6490LV scanning electron microscope was then performed, the results of which are presented in Figures 2 to 6.

In the samples subjected to tensile load very minor cracks have been found that were oriented mostly perpendicularly to the surface of the test bar. Cracks propagate preferentially in austenite in the samples in the as-received state (AR), or through the σ phase at the bound-

Table 3 **Test specimens load parameters**

AR		AN	
$R_{p0.2}$ /MPa	critical stress value / MPa	$R_{p0.2}$ / MPa	critical stress value / MPa
97	441	97	410
90	410	90	381
90	410	90	381
80	364	80	338
80	364	80	338
70	319	70	296

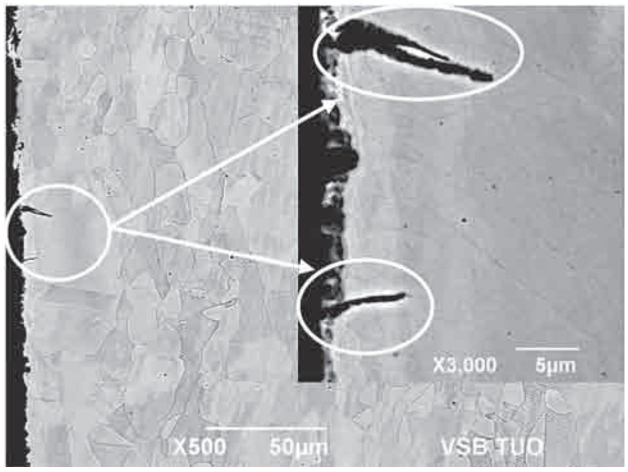

Figure 2 Sample AR, tension, 90 % $R_{p0.2}$ (410 MPa)

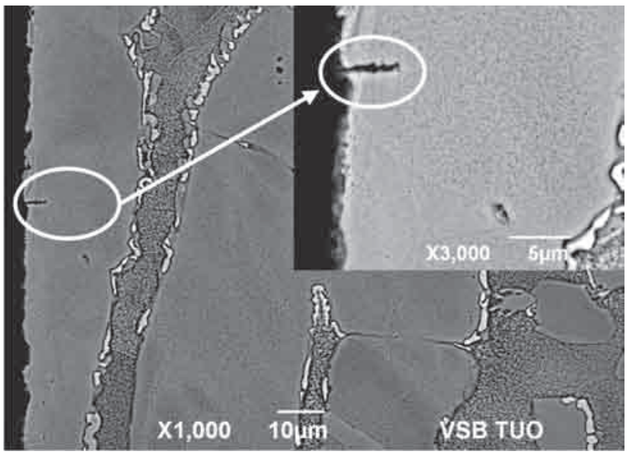

Figure 3 Sample AN, tension, 97 % $R_{p0.2}$ (410 MPa)

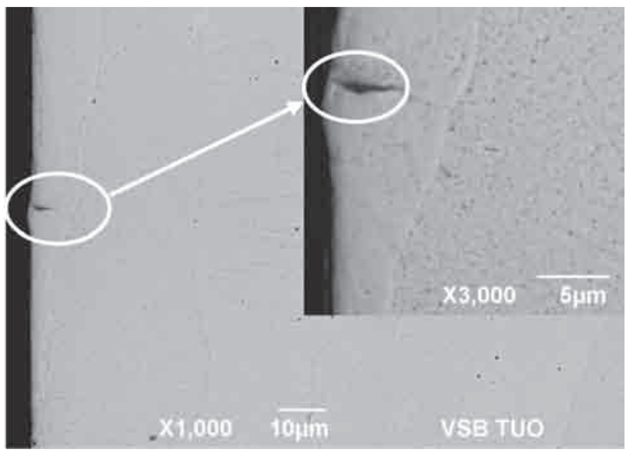

Figure 4 Sample AR, bending, 90 % $R_{p0.2}$ (410 MPa)

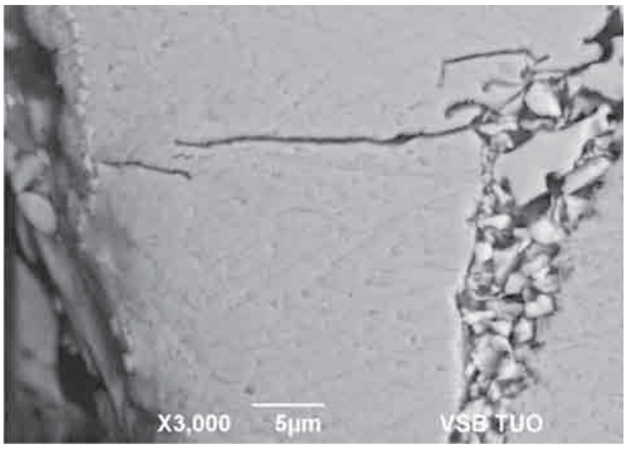

Figure 5 Sample AN, bending, 90 % $R_{p0.2}$ (381 MPa)

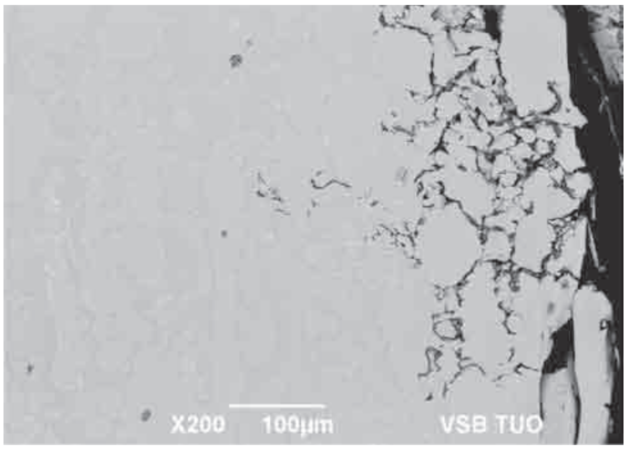

Figure 6 Sample AN, bending, 90 % $R_{p0.2}$ (381 MPa)

ary ferrite/austenite in the samples after laboratory annealing (AN). Occurrence of cracks in the state AN was more numerous than in the state AR. Length of cracks at both tested conditions did not exceed 15 μm. Characteristic images are shown in Figures 2, 3.

Similar character of damage as in the tensioned samples was observed also in the samples loaded by the four-point bending. The as-received state (AR) was again characterized by the occurrence of minor cracks running perpendicularly to the sample surface and extending to a depth of approx. 5 μm in the area of austenite (Figure 4). The cracks propagated in the samples in the state after laboratory annealing (AN) mainly at the interface of ferrite and austenite, i.e. in the areas of occurrence of the σ phase (Figure 5). The length of cracks varied around 100 μm. Areas with strong corrosive attack at the places of occurrence of the σ phase were also found, and minor cracks penetrated from them both through ferrite and austenite (Figure 6). The depth of corrosion attack from the surface of the sample was even approx. 400 μm.

CONCLUSIONS

The aim of this study was to evaluate the effect of testing methodologies and changes of microstructural parameters of duplex ferritic-austenitic steel resistance to SSC.

The steel was tested in two different structural states. It was the as-received state (AR) and the state after laboratory annealing performed by the mode 800 °C/5h/air (AN). Microstructure of steel in the AR state was formed by ferrite (approx. 60 %) and austenite (approx. 40 %). An intense precipitation of brittle σ phase at the boundary ferrite/austenite was observed in the state AN.

The volume fraction of the σ phase was approximately 8 %, and the distribution was homogeneous throughout whole volume of the sample.

The test specimens were loaded in accordance with the ASTM G49-85 and ASTM G39-99 Standards. Altogether 24 specimens were tested - 12 tensile test specimens and 12 four-point bend specimens.

For an objective comparison of both testing methods the same parameters of loading were chosen. During the standard time of testing (720 hours) not a single test specimen did break and also no surface defects were detected by examination of these specimens by stereomicroscope at the tenfold magnification. The studied duplex steel was thus resistant to SSC. Metallographic polished sections were then prepared on the exposed parts of the test specimens, which were subjected to evaluation by electron microscopy.

In the samples subjected to tensile load very minor cracks were found oriented mostly perpendicularly to the surface of the test bar. The cracks propagated preferentially in austenite in the samples in the as-received state (AR), or through the σ phase at the boundary ferrite/austenite in the state after laboratory annealing (AN). Occurrence of cracks in the state of AN was more numerous than in the state AR. Length of cracks at both tested states did not exceed 15 μm.

Similar character of damage as in the tensioned samples was observed also in the samples loaded by the four-point bending. The as-received state (AR) was again characterised by the occurrence of minor cracks running perpendicularly to the sample surface and extending to a depth of approx. 5 μm in the area of austenite. In the samples in the state after laboratory annealing (AN) the cracks propagated mainly at the interface of ferrite and austenite, i.e. in the areas of occurrence of the σ phase. Length of cracks was approx. 100 μm. Areas with significant corrosion attack were also found at the places of occurrence of the σ phase, from which minor cracks penetrated both the ferrite and austenite. The depth of corrosion attack from the surface of the sample was approx. 400 μm.

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Note: The responsible translator for English language is B. Škandera, Dobrá, Czech Republic